

**Zintl ions within framework channels: the complex structure and  
low-temperature transport properties of Na<sub>4</sub>Ge<sub>13</sub>**

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## Section S1. Interatomic Distances in the Na<sub>4</sub>Ge<sub>13</sub> crystal

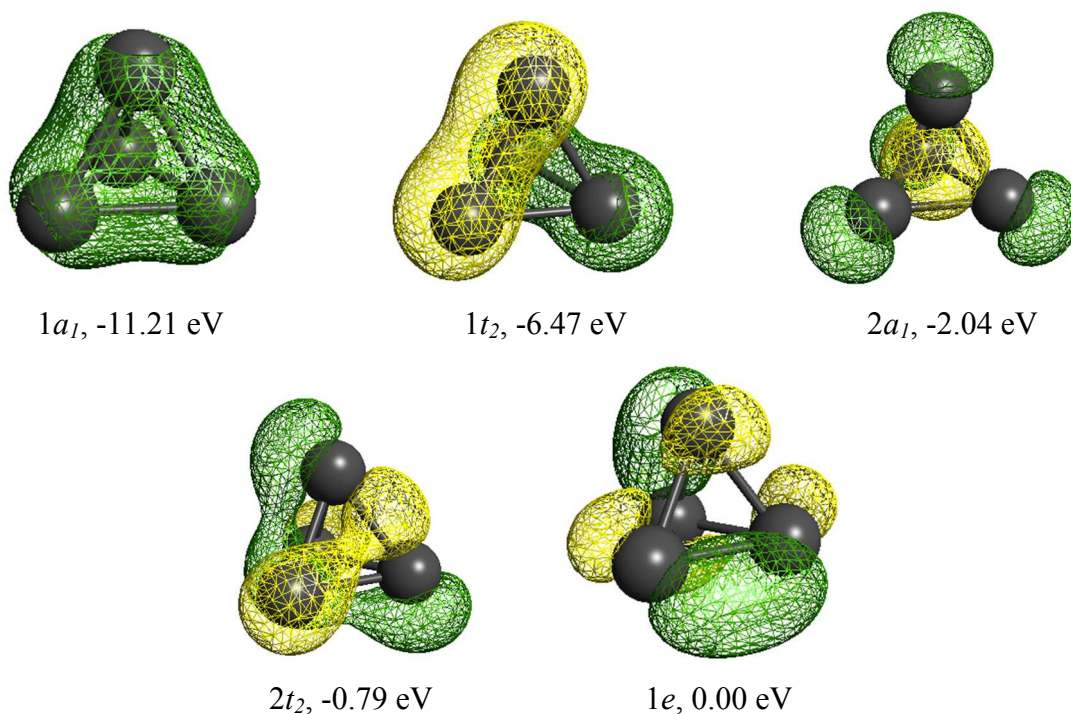
**Table S1.** Selected Interatomic Distances for Na<sub>4</sub>Ge<sub>12</sub>(Ge<sub>4</sub>)<sub>0.25</sub>

Interaction/Distance (Å)									
Ge1		Ge3		Ge5		Na1a		Na1b	
–Ge1*	0.733(7)	–Ge2	2.494(1)	–Ge3	2.497(1)	–Ge1*	2.754(5)	–Na1b*	0.496(12)
				x2					
–Ge1	1.474(2)	–Ge5	2.497(1)	–Ge4	2.512(1)	–Ge3	3.223(3)	–Ge1*	2.261(7)
x2*		x2				x2			
–Ge1	1.647(4)	–Na1b	3.178(5)	–Ge4	2.537(1)	–Ge3	3.236(3)	–Ge1*	2.766(7)
x2*		x2				x2			
–Ge6*	1.975(4)	–Na1b	3.210(5)	–Na2	3.221(1)	–Ge1	3.238(4)	–Ge1	3.134(6)
		x2		x2		x2			
–Na1b*	2.261(7)	–Na1a	3.223(3)	–Na1a	3.305(4)	–Ge5	3.305(4)	–Ge1	3.159(6)
		x2							
–Ge6	2.415(4)	–Na1a	3.236(3)			–Ge2	3.461(4)	–Ge1	3.171(6)
		x2							
–Ge6	2.523(4)	–Na1b	3.474(6)					–Ge3	3.178(5)
		x2							
–Ge1 x2	2.553(4)							–Ge3	3.210(5)
–Na1b*	2.590(6)							–Na1b	3.275(5)
								x2*	
								–Ge6	3.276(6)
Ge2		Ge4		Ge6		Na2			
–Ge4 x2	2.460(1)	–Ge2	2.460(1)	–Ge6*	0.599(8)	–Ge4	3.196(1)		
		x2				x6			
–Ge2	2.464(1)	–Ge5	2.512(1)	–Ge1	1.975(4)	–Ge5	3.221(1)		
				x6*		x6			
–Ge3	2.494(1)	–Ge5	2.537(1)	–Ge1	2.415(4)				
				x6					
–Na1a	3.461(1)	–Na2	3.196(1)	–Ge1	2.523(4)				
		x2		x6					
		–Na1a	3.239(4)						

\*These distances appear in the cif file for the fully occupied channel, but are not statistically possible based upon the proposed disorder. For Ge1, only one of the two possible interactions

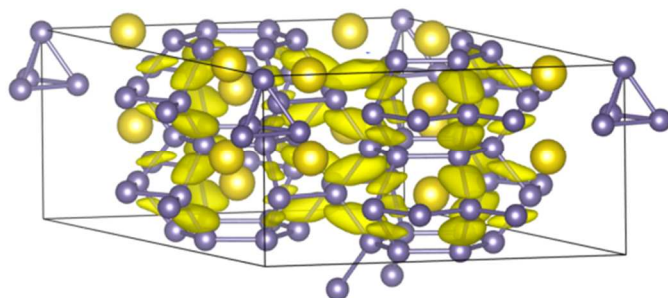
with Ge6 will occur at any given site. For Ge6, only three of the possible twelve interactions with Ge1 will occur at any given site.

## Section S2. Molecular orbital and bonding analysis

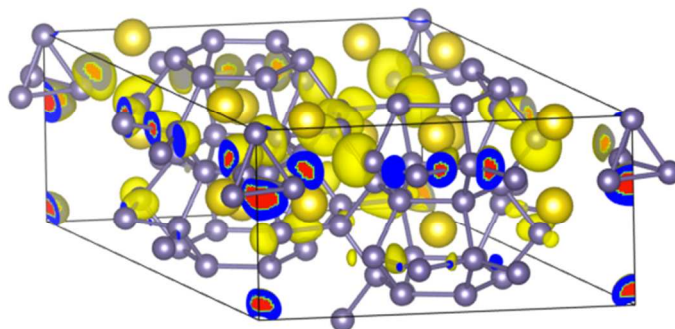


**Figure S1.** Valence occupied molecular orbitals of  $[\text{Ge}_4]^{4+}$ . Their energies are measured with respect to the highest occupied  $1e$  orbitals.

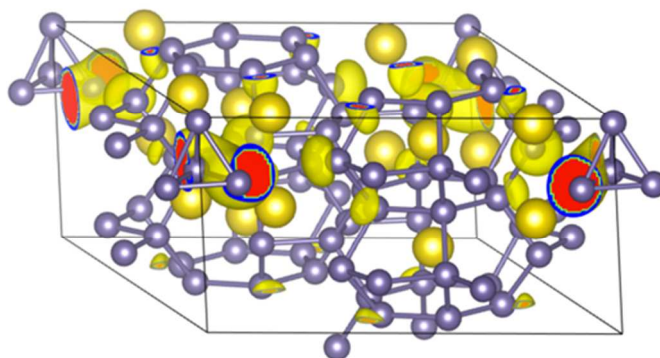
A few highest occupied crystal orbitals of the  $c \times 2$  structure at the  $\Gamma$  point have their densities shown in Figure S2. In the second and third highest occupied crystal orbitals (HOCO), HOCO-1 and HOCO-2, we can see some contributions from the tetrahedra. They do not exactly look like the  $1e$  and  $2t_2$  orbitals. However, with a slight distortion of the  $T_d$  structure, the two orbitals mix and contribute to the extended orbitals.



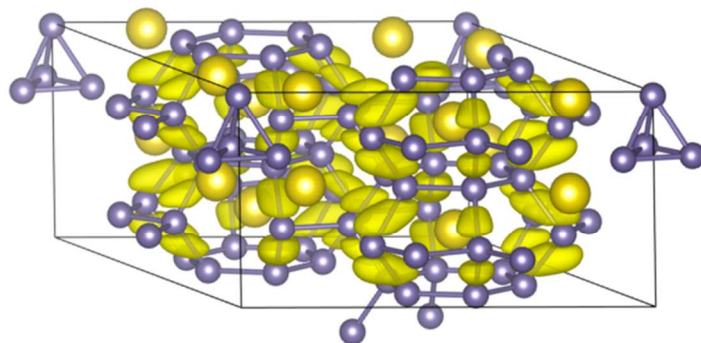
HOCO – 3 (2-fold degenerate)



HOCO – 2



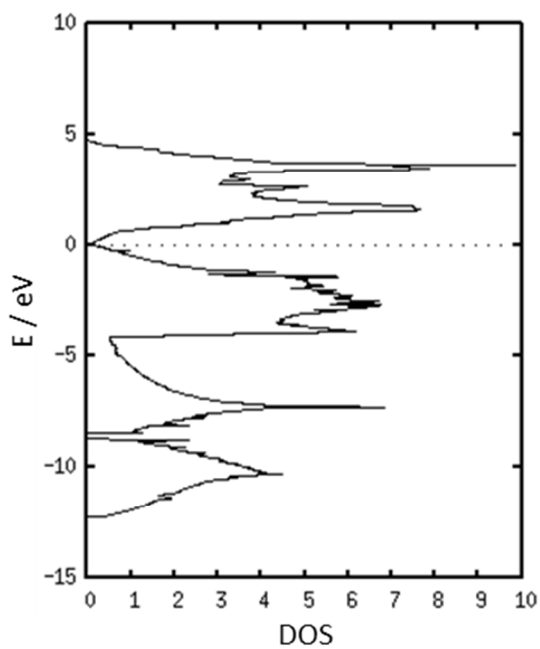
HOCO – 1 (2-fold degenerate)



HOCO

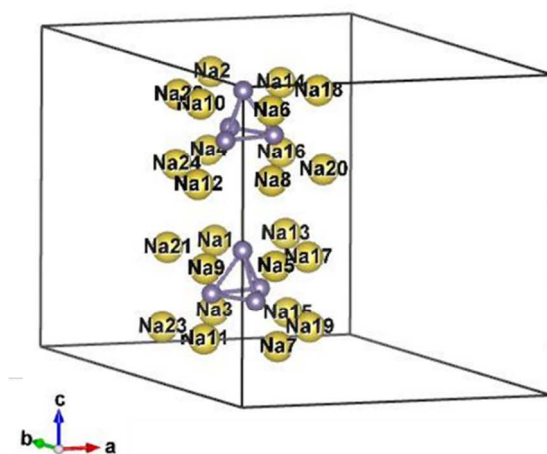
**Figure S2.** Densities of the three highest occupied orbitals (HOCO) of  $c \times 2$  at the  $\Gamma$  point.

$d$ -Ge is a poor conductor with the conduction and valence bands touching with DOS = 0 (Figure S3). The ionic interaction with the  $\text{Na}^+$  and the  $3c$   $\text{Ge}^-$  opens the band gap slightly to 0.16 eV and stabilizes the  $c \times 2$  structure.



**Figure S3.** DOS of  $d$ -Ge. Fermi level is set to be 0 eV.

*Staggered versus eclipsed configurations*



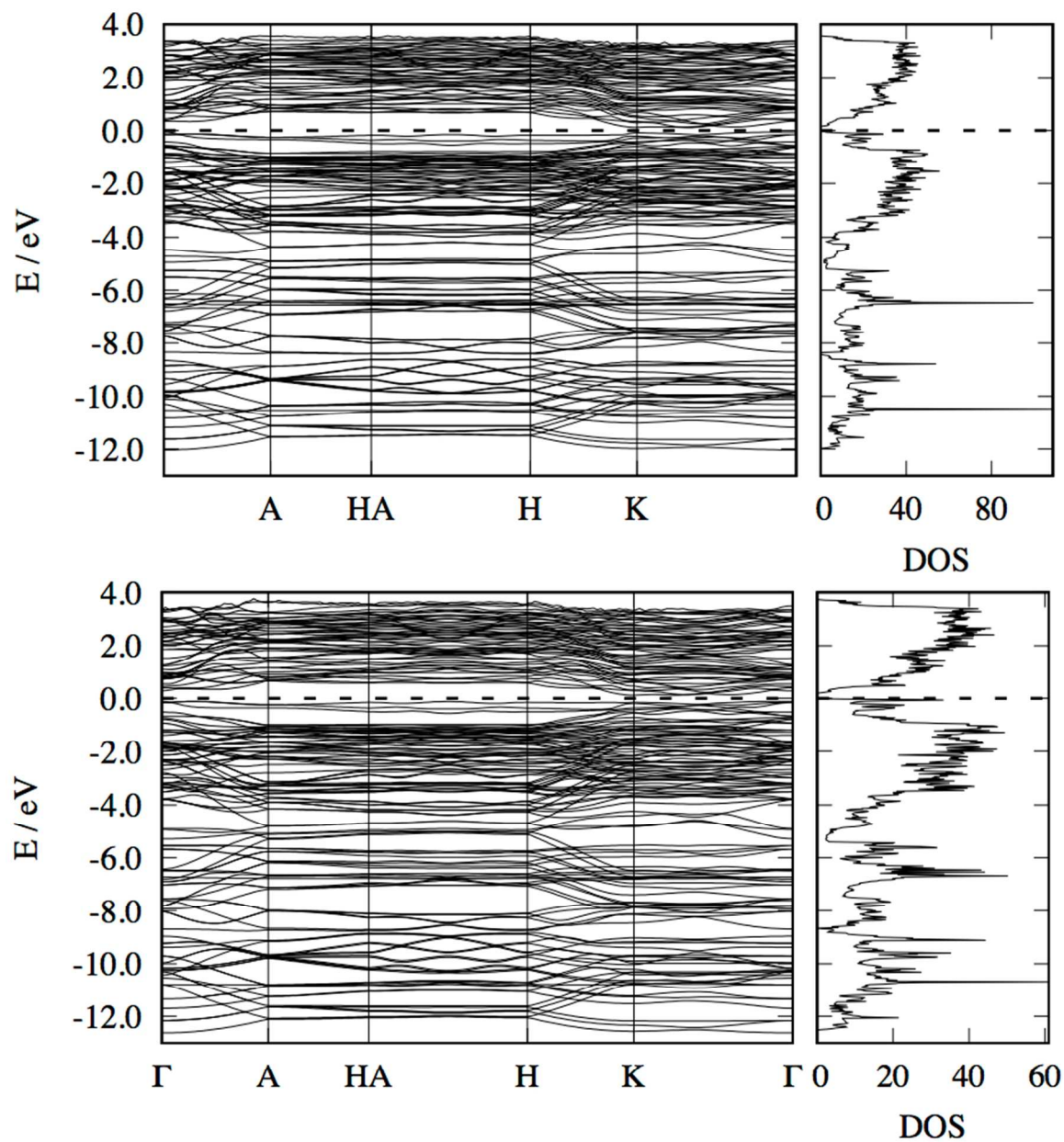
**Figure S4.** The cut-out of the atoms within the large channel in the staggered  $c \times 4$   $\text{Na}_{32}\text{Ge}_{104}$  unit cell. The Na atoms are labeled by numbers.

In each of the four 6-membered Na rings, there are two symmetrically unique Na atoms. From top to bottom, their distances to the  $c$ -axis are: 3.66 Å for Na2, 3.18 Å for Na6, 3.91 Å for Na12, 3.26 Å for Na16, 3.18 Å for Na1, 3.67 Å for Na5, 3.27 Å for Na11, and 3.90 Å for Na15. Certainly, as one Ge<sub>4</sub> tetrahedron rotates about the  $c$ -axis to be staggered to the other tetrahedron, the Na rings undergo a significant distortion, by  $\sim 0.5$  Å radially to the  $c$ -axis, to accommodate the rotation. Without such a distortion, the staggered configuration is significantly higher in enthalpy than the eclipsed by 2.70 eV / unit cell. The associated large amplitude distortion of the Na rings kinetically hinders the eclipsed-to-staggered conversion of the tetrahedra arrangement.

**Table S2:** Select Ge-Ge distances in Na<sub>4</sub>Ge<sub>13</sub> and their corresponding crystal orbital Hamilton populations integrated to the Fermi level (–ICOHP).

pair	Distance (Å)	–ICOHP (eV / bond)
Ge1-Ge1	2.60	2.84
Ge1-Ge6	2.66	2.68
Ge2-Ge2	2.51	3.77
Ge2-Ge3	2.52	3.99
Ge2-Ge4	2.51	4.11
Ge3-Ge5	2.55	3.78
Ge4-Ge5	2.56,2.59	3.97, 3.57

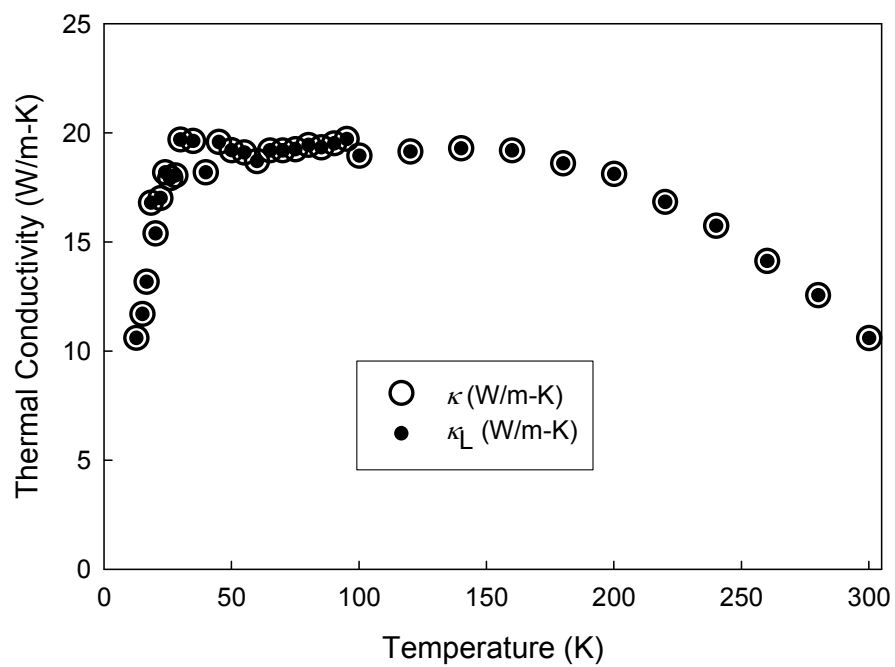
Section S3. Calculated Band Structures and Densities of States of the  $\text{Na}_{16}\text{Ge}_{52}$  unit cell.



**Figure S5.** Band structure and DOS of the  $c \times 2$   $\text{Na}_{16}\text{Ge}_{52}$  structure at 1 atm (upper panel) and 4 GPa (lower panel). They have been shifted so that the Fermi energy is at 0 eV.



#### Section S4. Thermal Conductivity of $\text{Na}_4\text{Ge}_{13}$ .



**Figure S6.** Total thermal conductivity,  $\kappa$  (open circles), and lattice contribution to the total thermal conductivity,  $\kappa_L$  (filled circles) for  $\text{Na}_4\text{Ge}_{13}$ .